Journal of Power Sources 225 (2013) 119–123

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Modification of the pore structures of fuel cell electrodes using a dry etching technique

Woon-Jo Kim [a,b], Asad Mehmood [a,d], Kwan-Young Lee [b,c], Heung Yong Ha [a,d,*]

[a] Energy Convergence Research Center, Korea Institute of Science and Technology (KIST), Hawolgok-dong 39-1, Seongbuk-gu, Seoul 136-791, Republic of Korea
[b] Department of Chemical and Biological Engineering, Korea University, Seongbuk-gu, Seoul 131-701, Republic of Korea
[c] Green School, Korea University, Seongbuk-gu, Seoul 131-701, Republic of Korea
[d] Department of Clean Energy and Chemical Engineering, University of Science and Technology (UST), Yuseong-gu, Daejeon 305-333, Republic of Korea

HIGHLIGHTS

► An ion-beam treatment has been employed to modify pore structures of electrodes.
► The etching of surplus ionomer turns catalyst layers highly rough and porous.
► Modification results in a substantial improvement of mass-transport processes.
► The ion-beam-treated MEAs exhibit improved performance for the DMFC.

ARTICLE INFO

Article history:
Received 1 August 2012
Received in revised form
20 September 2012
Accepted 12 October 2012
Available online 23 October 2012

Keywords:
Direct methanol fuel cell
Membrane-electrode assembly
Electrode structure
Ion-beam treatment
Electrode porosity

ABSTRACT

The anodes of membrane-electrode assemblies (MEAs) have been treated with an argon ion-beam under vacuum to etch out a part of the ionomer present in the catalyst layers. The ion beam treatment alters the surface morphology of the catalyst layer by promoting the pore size and overall porosity, which reduces the mass transport resistance of the reactants and the products through the catalyst layers. As confirmed, the electrochemical surface areas of the electrodes are not affected by the treatment, and the ion-beam-treated MEAs exhibit improved performance toward direct methanol fuel cells (DMFCs). Physical and electrochemical analyses have been carried out to characterize the modified electrodes in greater detail.

1. Introduction

The electrochemical reactions in fuel cells take place at the triple-phase boundary that consists of a catalyst particle, an ionomer and a reactant [1]. The triple-phase boundary and structure of the catalyst layer are strongly influenced by the electrode composition, which must be formulated precisely in terms of the choice of solvent, catalyst loading and ionomer content. Adequate morphology of the electrodes is critical to achieve a higher utilization of precious metal catalysts for better performance of the fuel cells. An adequate morphology even assists to reduce the catalyst loading with no significant deterioration in performance. In order to facilitate the diffusion of reactants to active sites and the removal of the products from the electrodes, high electrode porosity is another crucial requirement for a membrane-electrode assembly (MEA).

Many reports have dealt with the optimization of electrode structures by modifying the porosity and catalyst aggregate size. Kim et al. and others [2,3] have controlled the pore size of fuel cell electrodes by taking advantage of the dielectric properties of the solvents that were used to make catalyst inks [4,5]. Another approach modified the electrode structure by using carbonaceous materials as additives in the catalyst layers [6]. Liu et al. manipulated the electrode fabrication process to modify the anode porosity of a direct methanol fuel cell (DMFC), which promoted the mass transport of reactants and products [7].

* Corresponding author. Energy Convergence Research Center, Korea Institute of Science and Technology (KIST), Hawolgok-dong 39-1, Seongbuk-gu, Seoul 136-791, Republic of Korea. Tel.: +82 2 958 5275; fax: +82 2 958 5229.
E-mail addresses: hyha@kist.re.kr, hyha88@hotmail.com (H.Y. Ha).

0378-7753/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2012.10.042

One of the most frequently used methods has been the introduction of pore-forming agents in the catalyst inks to increase the electrode porosity [8,9]. These agents are then removed after MEA preparation using washing, heat treatment, or acid treatment processes. However, these additional steps are laborious, time consuming and can possibly increase the processing costs as well. Apart from that, the interfacial resistance between the electrodes and the membrane of the resultant MEAs can be increased during the processes that mostly include liquid phase extraction or evaporation under vacuum conditions. Also, there is a risk of electrode contamination if pore formers are not completely removed.

The methods mentioned above mostly include multiple steps that occur in the liquid phase. In the present study, we have adopted a different approach whereby a part of the ionomer is removed by a dry etching technique. The surfaces of polymeric materials can be modified by an ion-beam treatment technique under vacuum conditions [10,11]. Cho et al. [12] reported a method to modify the surface of a polymer electrolyte membrane (Nafion), which was then used to fabricate MEAs for polymer electrolyte fuel cells.

In this work, we used a novel and very effective technique, which proceeded under vacuum conditions to modify the pore structures of electrodes for fuel cells. The electrodes formed on the polymer electrolyte membrane were subjected to an ion-beam etching process in order to remove a part of the ionomer in the catalyst layer. The modified MEAs were characterized by using various physical and electrochemical techniques and their performance was tested for direct methanol fuel cells.

2. Experimental

Nafion® 115 (DuPont) was used as a polymer electrolyte membrane. PtRu/C (75 wt.%, HiSPEC 12100) and Pt/C (70 wt.%, HiSPEC 13100, Johnson Matthey Co.) were used as the anode and cathode catalysts, respectively. Catalyst inks were prepared by mixing respective catalyst powder, a 5 wt.% Nafion solution (DuPont) ionomer, de-ionized water and IPA in suitable proportions, and were then sonicated for 10 min to obtain well-dispersed catalyst inks.

The catalyst inks were directly sprayed onto the surface of the Nafion 115 membranes. The geometric area of the catalyst layer was 10.89 cm^2 with a loading of 2 mg cm^{-2} based on Pt metal weight for both anode and cathode. The ionomer content in each catalyst layer was 30 wt.% of the catalyst used. Hot-pressing was carried out under a pressure of 8 MPa at 140 °C for 5 min.

After fabricating the MEA, the anode catalyst layer was treated by an Ar^+ ion-beam under vacuum conditions of 8×10^{-5} kPa. The plasma was generated with argon gas while hydrogen gas was introduced to the vacuum chamber to make a hydrogen atmosphere at a flow rate low enough to maintain a predetermined vacuum level. Three different ion doses were used with an ion energy of 1.5 keV: 5×10^{16}, 1×10^{17}, and 5×10^{17} ions cm^{-2}.

The performance of the MEAs for DMFC was measured with a cell fixture having a serpentine flow field by using a commercial test station (Won-A tech, Korea). The DMFC tests were carried out at 60 °C and 1 atm, while supplying a 1.0 M methanol solution to the anode and air to the cathode. After single-cell testing, electrochemical analyses were conducted using a potentiostat (AutoLab, EcoChemie). Electrochemical impedance (EIS) of anode was measured at 0.4 V using a potentiostatic mode. Methanol solution with a concentration of 1.0 M was fed to the anode at 1 ml min^{-1} and humidified hydrogen was supplied to the cathode at 100 sccm, which functioned as a counter and reference dynamic hydrogen electrode (DHE) [13]. The frequency range was varied from 1 kHz to 0.1 Hz, and the amplitude of the applied AC voltage was 5 mV. Linear sweep voltammetry (LSV) was conducted to measure the anode overpotential for a methanol oxidation reaction (MOR) in a potential range of 0–0.8 V at a scan rate of 1 mV s^{-1}. Methanol stripping voltammetry (MSV) was carried out to analyze the electrochemical active surface area (ECSA) of the anode. For MSV measurement, methanol solution was fed to the anode for 20 min by holding anode potential at 0.1 V so that methanol can be adsorbed on the catalyst layer and then de-ionized water supplied to anode to remove the un-adsorbed methanol at the same holding potential. Afterward, adsorbed methanol was oxidized by cycling the anode potential between 0.1 and 0.7 V and MSV curve was recorded [14]. Morphological and structural characteristics of the anode catalyst layers were investigated using a scanning electron microscope (XL-30 FEG-ESEM, FEI Inc.). A mercury porosimeter (AutoPore IV, Micromeritics) was used to analyze pore structure of the pristine and ion beam treated anodes.

3. Results and discussion

Fig. 1 shows a schematic diagram of the change in the electrode morphology caused by an ion-beam irradiation that has the ability

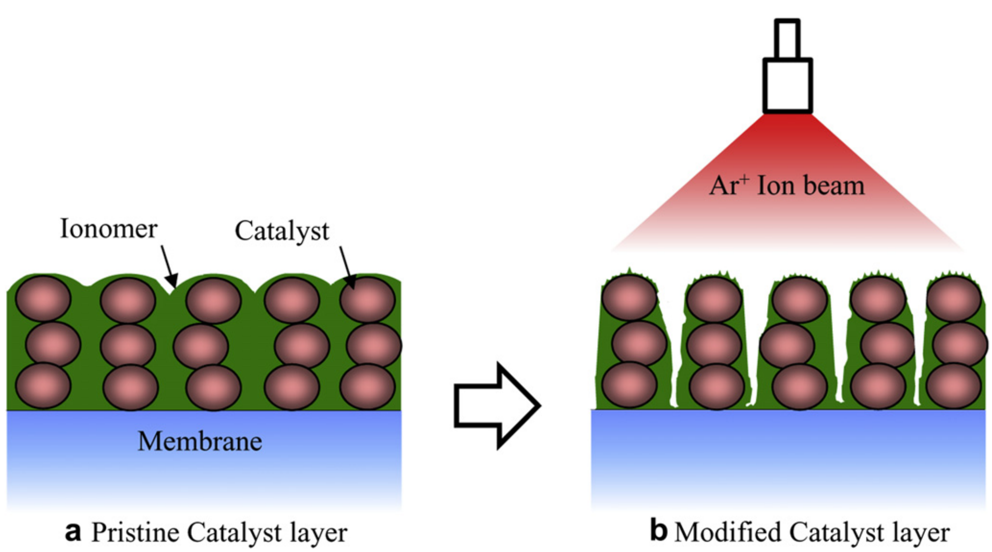

Fig. 1. A schematic diagram showing the change in the electrode structure by ion beam irradiation.

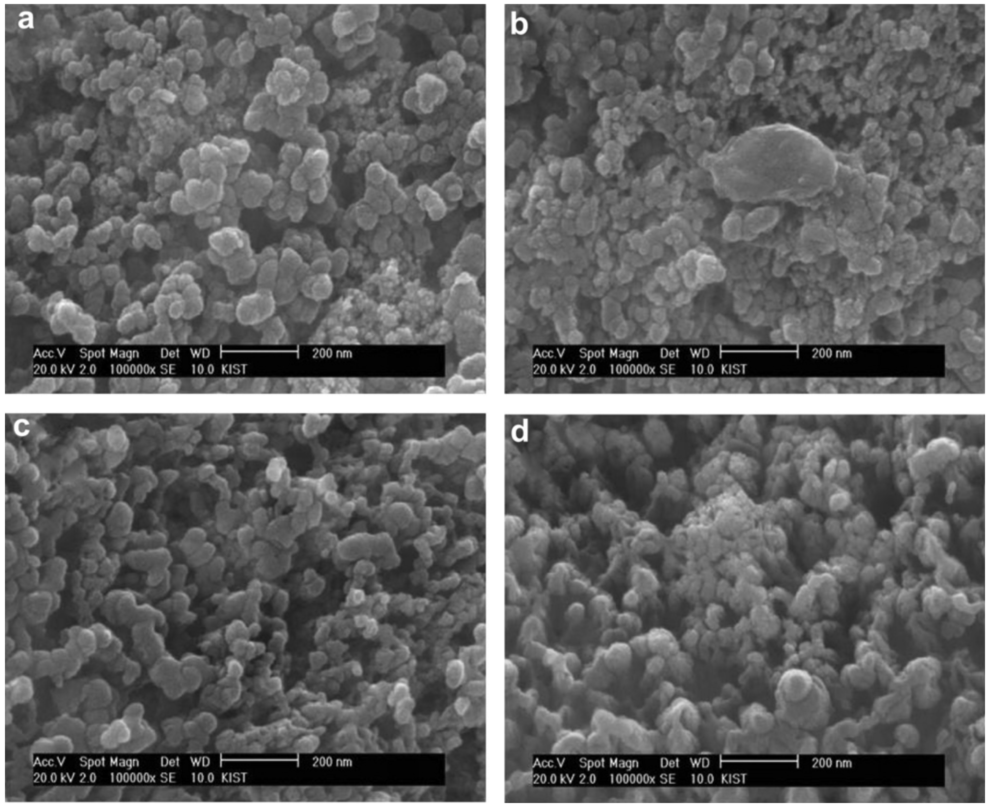

Fig. 2. SEM surface images of the (a) pristine and ion-beam treated catalyst layers with an argon ion dose of (b) 5×10^{16}, (c) 1×10^{17}, (d) 5×10^{17} ions cm^{-2}.

to etch polymeric materials leaving rugged surfaces [11,12]. The as-formed catalyst layers in DMFCs usually have a very small porosity because catalyst particles are abundantly covered by a polymeric ionomer that acts as both a binder and a proton conductor, as shown in Fig. 1a. When the catalyst layer is treated with an ion beam, then the polymeric ionomer from the surface can be partially etched away, which will improve porosity of the catalyst layers, as shown in Fig. 1b.

The anode catalyst layers comprised of PtRu/C and the ionomer were subjected to an argon ion-beam treatment at ion doses from 5×10^{16} to 5×10^{17} ions cm^{-2} under a hydrogen atmosphere. The SEM images of the electrodes before and after the treatment are shown in Fig. 2. In view of the pristine electrode (Fig. 2a), the catalyst particles seem to form large aggregates with the ionomer that acts as a binder, and the overall surface appears relatively compact with only small pores. When the electrode is treated with a low ion dose such as 5×10^{16} ions cm^{-2}, however, there is no appreciable morphological change. As the ion dose is increased to higher values of 1×10^{17} and 5×10^{17} ions cm^{-2}, substantial changes are observed in the surface morphology with a more rugged and porous catalyst layer. This is because a significant part of the ionomer is removed by the etching effect of the ion beam treatment. Such porous surfaces can assist in the effective channeling of reactants to the electrochemically active sites and can aid in the elimination of the products.

The pore size distribution data of the pristine and treated anodes are compared in Fig. 3. The primary pore region within a pore diameter of 0.1 μm exhibits no noticeable change in the pore volume for the pristine and treated anodes. However, for the secondary pores with a pore diameter of approximately 10 μm or higher, pore volume increases with the increase of ion dose. With a low ion dose of 5×10^{16} ions cm^{-2}, there is no appreciable change in the anode porosity but as the ion dose is increased to higher values, the secondary pore volume considerably improves and acquires highest value for an ion dose of 5×10^{17} ions cm^{-2}.

The MEAs with their anodes treated with different ion beam doses were tested in a DMFC at 60 °C at atmospheric pressure while supplying a 1.0 M methanol solution to the anode and air to the cathode. As shown in Fig. 4, the MEA treated with an ion dose of 5×10^{16} ions cm^{-2} exhibits the same performance as the pristine MEA. However, the performance improvement becomes more evident with the increasing ion dose and the highest power density of 117 mW cm^{-2} is obtained with the MEA treated with an ion dose of 5×10^{17} ions cm^{-2}. The improved performance may be attributed to the increased porosity of the anode catalyst layer, as shown in

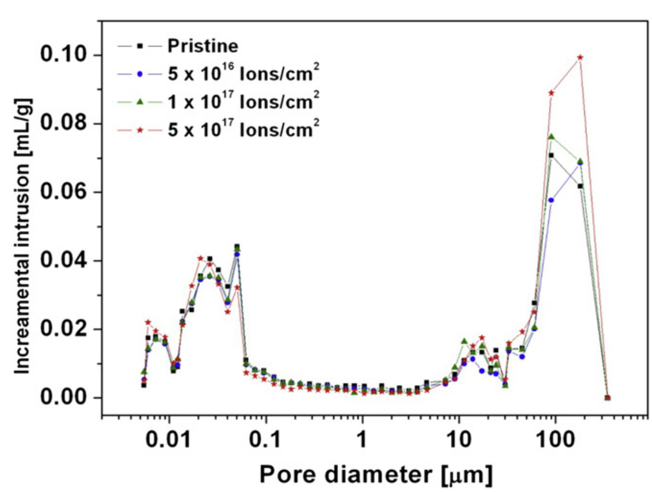

Fig. 3. Comparison of pore size distribution of the pristine and ion beam treated anode catalyst layers.

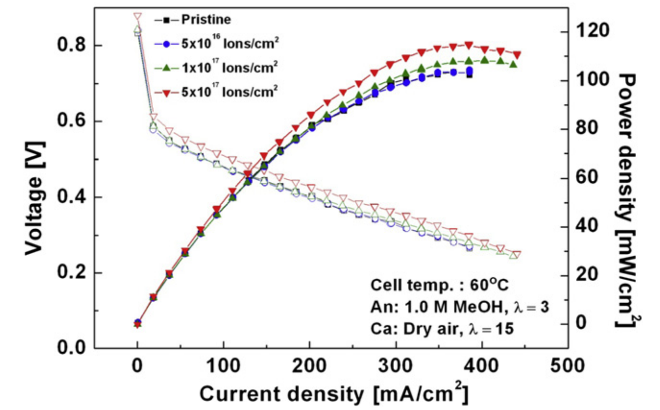

Fig. 4. DMFC performance of the pristine and ion-beam treated MEAs tested by supplying a 1.0 M methanol feed to the anode and air to the cathode at 60 °C and 1 atm.

Fig. 3, which facilitates the mass transport of the reactant methanol and the product CO_2 at the anode [7].

The electrochemical surface areas of the anodes were measured through methanol stripping voltammetry. As shown in Fig. 5, the methanol oxidation peaks appear in the potential range between 0.25 and 0.58 V (vs. DHE). MSV curves have an average peak area of 10 C for all MEAs with less than 2% variation and there is no shift of the onset and peak potentials for methanol oxidation curves of pristine and treated MEAs. Therefore, it is confirmed that the ion beam etching does not hamper either the electrochemical surface area or the catalyst activity. Only the surplus ionomer is removed from the catalyst aggregates, which has increased the porosity of the electrode and thus led to an improved mass transport of the reactants and products.

Electrochemical impedance analysis (EIS) and anode polarization of the methanol oxidation reaction (MOR) were also carried out for the MEAs to further characterize their electrochemical properties. As shown in the Nyquist plots of Fig. 6a, the MEAs treated with an ion dose of 1×10^{17} and 5×10^{17} ions cm^{-2} show a charge transfer resistance that is significantly smaller than that of the pristine MEA, thus exhibiting an enhanced activity toward the methanol oxidation reaction. Ohmic resistances for pristine and MEAs treated with ion doses of 5×10^{16}, 1×10^{17} and 5×10^{17} ions cm^{-2} are 0.64, 0.66, 0.66, and 0.52 Ω cm^2, respectively. Similar or lower ohmic resistances of the treated catalyst layers than that of the pristine one indicate that ionomer contents are sufficient in the treated catalyst layers to provide enough proton conduction paths. Only surplus ionomer is etched by ion beam which improved pore structure and resulted in high DMFC performance.

In addition, the anode polarization curves for MOR in Fig. 6b show that the MEA treated with an ion dose of 5×10^{17} ions cm^{-2} have a substantially lower anode overpotential compared with the pristine MEA. This difference is more pronounced particularly in high current density regions where performance is predominately governed by mass transport phenomena. This implies that the high anode porosity of a treated MEA uplifts the methanol accessibility to the three-phase boundary via an efficient removal of CO_2 bubbles that otherwise can hinder the diffusion of liquid methanol.

4. Conclusions

The anode catalyst layers of MEAs for DMFCs have been treated with argon ion beams to remove a part of the ionomer dispersed in the catalyst layer. The ion beam treatment alters the surface morphology of the catalyst layer by promoting the pore size and overall porosity. The modified MEA suffers no decline in the electrochemical surface area or catalyst activity, and exhibits improved performance for the DMFC. This is ascribed to the increased mass transport rates of the reactants and the products in the catalyst

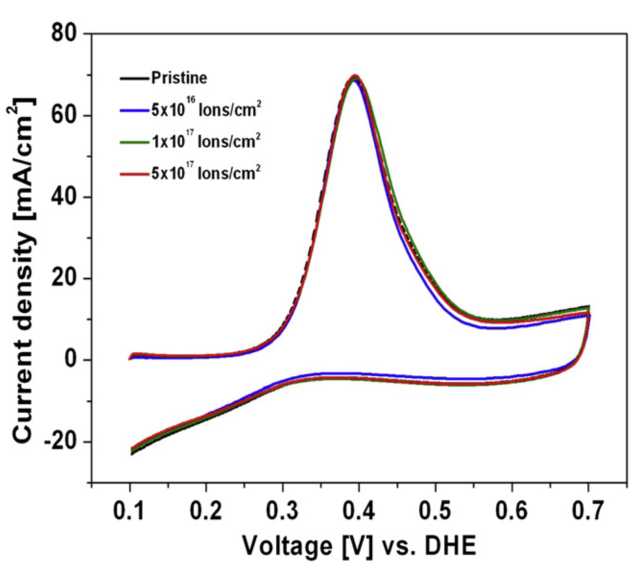

Fig. 5. Methanol stripping voltammograms for the anode of pristine and ion-beam treated MEAs.

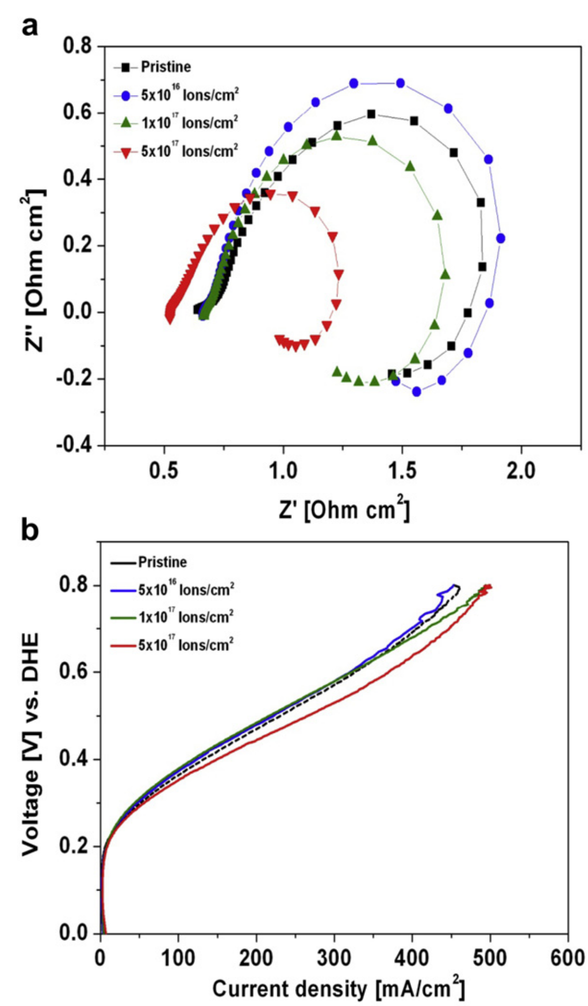

Fig. 6. Characterization of the MEAs through (a) electrochemical impedance analysis and (b) anode polarization curves for methanol oxidation reaction.

layer. Therefore, ion beam treatment is considered a very facile and effective method to modify the pore structure of electrodes, and to improve the performance of DMFCs.

Acknowledgment

This work was supported by a Korea CCS R&D Center (KCRC) grant funded by the Korea government (Ministry of Education, Science and Technology) (No. 2012-0008931) and also by the Korea Institute of Science and Technology under grant number (KIST-2E22842).

References

[1] R. O'Hayre, S.-W. Cha, W. Colella, F.B. Prinz, Fuel Cell Fundamentals, second ed., John Wiley & Sons Inc., 2009, pp. 97–98.
[2] J.-H. Kim, H.Y. Ha, I.-H. Oh, S.-A. Hong, Ho-In Lee, J. Power Sources 135 (2004) 29–35.
[3] R. Fernández, P. Ferreira-Aparicio, L. Daza, J. Power Sources 151 (2005) 18–24.
[4] M. Uchida, Y. Fuoka, Y. Sugawara, H. Ohara, A. Ohta, J. Electrochem. Soc. 145 (11) (1998) 3708–3713.
[5] S.-J. Shin, J.-K. Lee, H.-Y. Ha, S.-A. Hong, H.-S. Chun, I.-H. Oh, J. Power Sources 106 (2002) 146–152.
[6] S.-M. Park, D.-H. Jung, S.-K. Kim, S. Lim, D. Peck, W.H. Hong, Electrochim. Acta 54 (2009) 3066–3072.
[7] G. Liu, M. Wang, Y. Wang, F. Ye, T. Wang, Z. Tian, X. Wang, Int. J. Hydrogen Energy 37 (2012) 8659–8663.
[8] Z. Wei, S. Wang, B. Yi, J. Liu, L. Chen, W.-J. Zhou, W. Li, Q. Xin, J. Power Sources 106 (2002) 364–369.
[9] M.C. Tucker, M. Odgaard, P.B. Lund, S. Yde-Andersen, J.O. Thomas, J. Electrochem. Soc. 152 (2005) A1844.
[10] H. Dong, T. Bell, Surf. Coat. Technol. 111 (1999) 29–40.
[11] I.P. Jain, G. Agarwal, Surf. Sci. Rep. 66 (2011) 77–172.
[12] S.A. Cho, E.A. Cho, I.-H. Oh, H.-J. Kim, H.Y. Ha, S.-A. Hong, J.B. Ju, J. Power Sources 155 (2006) 286–290.
[13] T.V. Reshetenko, H.-T. Kim, H.-K. Lee, M.-Y. Jang, H.-J. Kweon, J. Power Sources 160 (2006) 925–932.
[14] J. Prabhuram, N. Nambi Krishnan, B. Choi, T.-H. Lee, H.-Y. Ha, Int. J. Hydrogen Energy 35 (2010) 6924–6933.